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# PATENT SPECIFICATION

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(19)

## (54) IMPROVEMENTS IN AND RELATING TO THE MANUFACTURE OF SHEET, OR FILAMENT, MATERIAL

(71) We, ROTHMANS INTERNATIONAL LIMITED (formerly Carreras Limited), a British Company of Christopher Martin Road, Basildon, Essex, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention is concerned with improvements in and relating to the continuous or semi-continuous manufacture of product material, and is particularly but not exclusively concerned with the case where the product material is used in or as smokeable material used, for example, to form binders or wrappers or filler material for smoking articles such as pipes, cigarettes, cigars, and the like.

It is known to provide smokeable material which includes calcium alginate in fibrous form. Thus, our U.K. patent specification No. 1,372,510 discloses and claims a smokeable material comprising a base material together with additional material which provides both a minor proportion of flavouring agent and a combustion modifier, the additional material being incorporated so as to communicate flavour to and to allow the burning of the smokeable material in such manner as to render the smokeable material suitable for use in place of smoking tobacco, in which the base material is calcium alginate in fibrous form. The additional material may comprise cellulosic fibres, a colouring agent such as FDC 1596 Brown, nicotine or a salt of nicotine, citric acid, certain flavouring material such as powdered deer tongue, certain burning-sustaining material such as sodium nitrate, tobacco.

That specification also provides and claims a method of manufacturing such smokeable material, by specified steps including the use of the web-forming unit of a paper-making machine, from calcium-alginate fibres. Such fibres may be obtained from seaweed by steps including the step of forming those fibres by squirting an aqueous solution of a water-soluble alginate into an aqueous solution of calcium chloride.

It is known to manufacture so-called "reconstituted tobacco sheet" (which, be it noted, essentially contains tobacco) by a number of different processes which do not involve the use of the web-forming unit of a papermaking machine.

One such said different process may be referred to for convenience as "the band tobacco process". In the band tobacco process, tobacco powder is obtained in a dry or substantially dry state: the tobacco powder may derive from waste material ("offal"), or may derive from tobacco leaves or stems which may or may not be low-quality tobacco; moreover, different kinds of tobacco may be present in the tobacco powder, as the process lends itself to intimate blending. The process usually involves forming an aqueous slurry of the tobacco powder and (usually) an adhesive binder, and feeding the slurry on to a moving belt whereon it takes the form of a self-coherent tobacco-carrying thin layer; heat is supplied to the layer to convert it into a self-supporting sheet which may be moistened to permit it to be stripped from the belt; thereafter, the sheet may be reeled into a roll or may be cut-up into small pieces. It is known that, as a modification, the said feed of the slurry may be by extrusion and so as to form filament material instead of sheet material: see, for example, United States patent No. 2,613,673 at column 6 lines 23—31.

Thus, U.K. patent specification No. 815,315 appears to disclose various methods for manufacturing reconstituted tobacco sheet by the band tobacco process. It appears that the basis of the arrangements disclosed is, that pulverised tobacco is mingled with "an initially

substantially water-insoluble adhesive" to form a slurry which is spread out into a layer which is dried to form the reconstituted tobacco sheet, it being stated that "the term 'initially substantially water-insoluble adhesive' is intended to define an adhesive which at one stage in the manufacture of the tobacco sheet, i.e. before forming or drying the sheet, is substantially water-insoluble", and it being also stated that "initially water insoluble material does not form a true solution but may be applied in a gelatinous and dispersed condition to tobacco particles". As an example of such an arrangement, the Example 4 describes the preparation of an aqueous "binder mixture" comprising a *colloidal dispersion* of *(water-insoluble)* calcium alginate in the presence of (a stoichiometric excess of *water-soluble)* sodium alginate: this "binder dispersion" is mixed with cigarette paper pulp fibre and then mingled with ground tobacco: the resulting "suspension" is passed twice through a colloid mill, to form the slurry mentioned above. It is further stated that "in the finished tobacco sheet the adhesive formulation may be between 0.5% and 33% by weight but a preferred range is between 1% and 20%."

U.K. patent specification No. 1,157,574 appears to disclose methods of forming reconstituted tobacco sheet in a somewhat different manner. In this case, apparently, pulverised tobacco may be suspended in an aqueous solution of a *water-soluble* alginate (sodium alginate, in Examples 11 and 12): a selected multi-valent cation (e.g. calcium, supplied as calcium citrate) is then so introduced that a *gel* of *water-insoluble* alginate (e.g., calcium alginate) forms in such a controlled manner that the tobacco becomes trapped within the gel. This gel is then rolled and dried, to form the reconstituted tobacco sheet.

Belgian patent specification No. 687,507 appears (from a translation into English) to make a number of proposals (but does not disclose any precise methods) relating to the manufacture of products to be smoked. The patent apparently proposes to employ, as structural substances of a product to be smoked, which substances "during the process of combustion, contain the least harmful ingredients in the smoke", the following substances: "Cellulose which is as pure as possible (alpha-cellulose) or the ester of cellulose, regenerated cellulose, viscose, other polycarbohydrates such as alginates, and, to a certain extent, non-combustible synthetic substances such as polyvinyl alcohol or polyolefines".

Apparently, these structural substances are to be impregnated or humidified by solutions obtained by the extraction of tobacco. Further, it is apparently proposed that these structural substances may be in a variety of physical forms: these forms include, for example, fibres, threads, filaments, powder, foams, sponges, tissues, tapes, films, and gauze. In addition, apparently, further materials (of which a large number are listed) may also be incorporated into the product to be smoked.

Another such said different process, which also does not involve the use of the web-forming unit of a papermaking machine, may be referred to for convenience as "the rolling-forming process". In one form of this case, tobacco powder is obtained in a dry or substantially dry state (as mentioned above in connection with the band tobacco process) and is mixed with suitable quantities of an adhesive binder and (where required) of an humectant, and sufficient water is added to enable the homogeneously mixed mass to be rolled into an extensive elongate self-supporting sheet by the action of a series of rolling-mills: thereafter, the sheet is dried by heat to a desired moisture-content, whereafter the sheet may be rolled up onto a bobbin or, alternatively, cut or shredded into pieces of a suitable size for further processing.

According to one aspect of the present invention there is provided a method of manufacturing product material including the steps of producing a mix including a water-insoluble alginate in a divided state and liquid medium, forming a thin (as hereinafter defined) elongate mass from the mix by means not including the use of a web-forming unit of a papermaking machine and removing any surplus of the liquid medium from the thin mass, whereby to form with a required moisture-content the product material, in which the divided alginate comprises fibres or fibrous material or material derived by mechanical division of fibres or fibrous material.

The expression "thin" is intended to refer to material having a thickness of the order of magnitude of the thickness-range of paper or paperboard as normally manufactured.

The liquid medium may be water. Conveniently, the mix contains also an adhesive binder.

The product material may comprise sheet material or filament material. The water-insoluble alginate may be calcium alginate.

It is in this case, where the water-insoluble alginate is calcium alginate, that we contemplate that the product material shall be used (with or without tobacco) in or as smokeable material.

In selecting calcium alginate as the basis of a smokeable material, we have given attention to the class of alginates and to the various forms in which the alginates can occur.

We have selected calcium alginate because our investigations lead us to believe that it provides a unique combination of advantages as follows:—

1) The inorganic content of calcium alginate, which is approximately 10% in itself, lowers the proportion of smoke (as particulate "tar" and gas phase) which will be delivered on

combustion, and is present as calcium which is potentially non-toxic. (The human body contains a high proportion of calcium, and other products which are applied internally and externally to the human body contain calcium in significant quantities, e.g. plant and animal products). All other radicals which form water-insoluble inorganic derivatives of alginic acid are or may be toxic, either per se and/or as regards their contribution to the smoke.

2) Calcium alginate can be made readily and relatively cheaply in fibrous or other forms in comparison with other alginates because of the availability of seaweed and the availability of calcium chloride as waste material of other industrial processes.

3) Calcium alginate can be given a tobacco-like appearance.

4) Calcium alginate can be made smokeably burnable by reasonable amounts of additional material.

5) Calcium alginate in fibrous form can be made into sheet by papermaking processes during which the calcium alginate tends to become purified and which permit a product of suitable porosity, basis weight and other physical characteristics to be obtained. Such sheet may be utilised to obtain the divided calcium alginate in the mix of the present invention.

Thus, in the case of calcium alginate, the present invention conveniently includes the step of incorporating into the product material at any stage of the said manufacture or subsequently, additional material so as at least to flavour the product material and to improve its burning characteristics.

Conveniently, at least some of the additional material is incorporated into the mix.

The additional material may consist of or include tobacco in a divided state.

Alternatively or in addition, the additional material may comprise at least one of a filler, an humectant, a colouring agent, an agent for supplying nicotine, an agent for modifying the action of nicotine, an agent for flavouring, an agent for sustaining burning, a combustion catalyst, a plasticizer, a wetting agent, a hardener, all as generally known in the tobacco art or as referred to herein.

Conveniently, at least a part of the any surplus liquid medium is removed with the aid of heat. However, at least a part of the any surplus liquid medium may be removed without the aid of heat.

Conveniently, the mix is poured, or extruded, as a step of forming the product material.

The invention may be put into practice in a number of ways, but two specific embodiments and a number of modifications thereof will now be described with reference to the accompanying drawings in which:—

Figs. 1 and 2 respectively illustrate two different methods of manufacturing the product material according to the invention.

In one arrangement, the mix is metered on to a support surface to form the thin mass, and the any surplus liquid medium is then removed so as to convert the thin mass into a self-supporting form. Fig. 1 indicates, semi-diagrammatically, one such an arrangement.

Referring to Fig. 1, the flow sequence (in the case where tobacco is included) is as follows:—

Tobacco 1 (of one or more kinds, and particularly but not exclusively tobacco leaves or stems or ribs or stalks which may or may not be low-quality tobacco) which is of too large a size to be fed directly to a wet-grinding stage, is first granulated to a suitable smaller size and may then be mechanically blended (if any required blending is not performed entirely at a later stage) and thereafter ground fine to a meal.

Tobacco which is not initially of the large size, particularly but not exclusively waste material such as "offal", may either be introduced at an appropriate point in the just-described sequence or, if it is fine enough, may be used directly.

The dry tobacco obtained by one or other or both of the above procedures is then mixed (as at 2) with water 3, with (if provided) the adhesive binder 4 (for example, the sodium salt of carboxymethyl cellulose), with calcium alginate 11, and with (if provided) any other additional material 100 (see below).

The mixing is accompanied by such further mechanical division, as by grinding, as may or may not be necessary to produce the required aqueous slurry (mix).

The calcium alginate 11 is in the form of fibres, which may or may not have been mechanically divided (conveniently while dry or substantially dry). The arrangement may be such that the calcium alginate in the aqueous slurry (mix) is pulverized, with a particle-size similar to that preferred for the tobacco in the slurry, of the order of magnitude of 50 microns.

During the above-mentioned steps, suitable ball mills, colloid mills, grinders, pulverizers, and/or mixers, and the like, may be employed as appropriate.

The aqueous slurry (mix) is metered by any suitable means 5, for example poured via an outlet valve 12, on to a suitably impermeable and non-reactive support surface such as, for example, an endless moving belt 6. The slurry is laid upon the belt in the form of an appropriately thin self-coherent layer (mass) and is conveyed, by the belt, to and past suitable drying apparatus 7 (for example, air jets or an oven or infra-red heaters or a suction pump or vacuum pump) which acts to remove the said any surplus water to convert the thin layer into a self-supporting sheet

(for example, a foil) with a required moisture-content, which sheet will tend to be of lesser thickness than the thin layer and which sheet may be moistened (as by a spray 8) if required to permit it to be stripped from the belt (as by a roll 9 or the equivalent doctor blade), whereafter the sheet may be reeled into a roll 10 or may be shredded (or otherwise mechanically divided) into small pieces (for example, flakes).

We contemplate that the slurry may incorporate, instead of the water, another liquid medium which is preferably neutral by nature.

The metering may be performed by any suitable means, for example by metering rolls (as, for example, a "reverse roll coater" comprising co-operating casting and doctor rolls), or by a levelling box and doctor blade, or by extrusion, or by spraying, or by pouring (as above), or by spreading-out, or by centrifugal application, or by pressing, or by rolling, or by any other means.

It will be clear that, instead of manufacturing the said product material in the form of sheet material, it may instead be similarly manufactured in the form of filament material.

Instead of an endless belt moving relatively to the metering means and to the drying apparatus, other mechanically equivalent arrangements may be employed.

The support surface (for example, the endless belt) may be made of stainless steel or be chromium-plated. It conveniently has a horizontal run. Where the metering means meters a single thin layer on to the forming surface, the width of that surface (for example, the width of the belt) is selected to be suitable to the desired width(s) of the thin layer and of the product sheet. In modifications, the metering means may be arranged to simultaneously meter more than one thin layer on to the forming surface (for example, the endless belt), or may be arranged to simultaneously meter at least one thin layer on to each of a plurality of parallel-arranged forming surfaces (each, for example, in the form of the endless belt); in such cases, the width(s) of the forming surface(s) is or are selected appropriately.

The speed of the moving endless belt (or the relative speed of the equivalent forming surface), the rate of metering of the slurry, the rate of operation of the drying apparatus, and the rate of any said moistening of the sheet, are correlated to produce the desired sheet.

In the formation of the slurry, a limited quantity of the water is employed, so as to tend to avoid leaching of the solubles from the tobacco, to tend to avoid any unwanted hydration of other materials present in the slurry, and to tend to avoid the necessity of subsequent removal of large quantities of the water by the drying apparatus.

Where the adhesive binder is at least in part water-soluble to form aqueous material, the viscosity of such aqueous material at its introduction to the mix may have a relatively low value of the order of magnitude of 50 centipoises but the invention is not limited to such low viscosities.

The divided calcium alginate in the aqueous slurry (mix) comprises fibres or fibrous material or material derived by mechanical division of fibres or fibrous material. Possible origins of such fibres or fibrous material, i.e. the raw material, are discussed below. We contemplate in particular (see below) that the calcium alginate 11 shall be derived by mechanical division (conveniently while dry or substantially dry) of fibrous sheet material.

Whether or not the tobacco 1 is included, the other additional material 100 may be included if and as required and may comprise at least one of a filler, an hemectant, a colouring agent, an agent for supplying nicotine, an agent for modifying the action of nicotine, an agent for flavouring, an agent for sustaining burning, a combustion catalyst, a plasticizer, a wetting agent, a hardener, all as generally known in the tobacco art or as referred to herein.

In the cases where the said product material does not include tobacco and/or does not include an adhesive binder and/or where the alginate is not calcium alginate, the procedure is generally similar to that just described, with modifications as appropriate.

## EXAMPLE 1.

The manufacturing method of Fig. 1 is illustrated by the following bench-scale experiments.

## EXAMPLE 1(A)

30g. of anhydrous sodium-alginate powder was dissolved in 2 litres of cold distilled water with vigorous agitation, using a "Silverson" (Registered Trade Mark) mixer, to give a viscous solution ("Solution A").

22g. of anhydrous calcium-chloride was dissolved in 2 litres of cold distilled water, to give a clear solution ("Solution B").

500ml. of "Solution A" (above) was agitated vigorously with the "Silverson" mixer equipped with a fine-mesh screen, and 500ml. of "Solution B" (above) was added slowly during the agitation, to produce a fine suspension of precipitated calcium alginate ("Product C") from the initially formed fibres. 200ml. of this suspension was evaporated under vacuum, using a rotary vacuum evaporator, to a volume of approximately 40ml., to convert it to a slightly viscous slurry (mix).

A film of this slurry was spread, using a scraper doctor bar, on to a flat metallic surface, and was allowed to condition in a humidity cabinet (set at 19°C, 60% relative humidity) for 4 hours. The slurry had then lost

sufficient moisture by evaporation, to form a thin, self-coherent, slightly translucent film, or foil, which, although not completely dry, was quite strong in tension. When ignited in a cigarette-lighter flame, small samples of this film smouldered for a short while, did not erupt into flame, and the smouldering could be modified by suitable known additives.

## EXAMPLE 1(B)

10g. of repurified calcium-alginate fibre (type CA—33 ex Alginate Industries Ltd, see below) was dispersed in 200ml. of distilled water in a bench-scale liquidiser to form a smooth fibre dispersion, or stock.

200ml. of calcium-alginate dispersion ("Product C" from Example 1(A) above) was taken, and was added to 50 ml. of the fibrous calcium-alginate stock made above, and dispersed evenly by hand stirring.

This dispersion was then stripped to ca.40ml. volume by means of a rotary vacuum evaporator, to produce a slightly viscous slurry (mix). A sample of this slurry was scraped onto a flat metallic surface, and was allowed to lose moisture by evaporation in the humidity cabinet under conditions as set out in Example 1(A) above. The product was a thin, slightly translucent, self-coherent film, in which the dispersion of fibres was quite easily visible; it was of good tensile strength, and had combustibility properties similar to those of the Example 1(A) product above.

In an alternative arrangement according to the invention, the material of the mix is converted by passage between rolls into a self-supporting form, the liquid medium incorporated into the mix being sufficient to permit such conversion. Fig. 2 indicates, semi-diagrammatically, one such an arrangement.

Referring to Fig. 2, the flow sequence (in the case where tobacco is included) is as follows:—

Tobacco is prepared similarly to that at stage 1 of Fig. 1; thus, for example, three different kinds of such tobacco may be so prepared and stored respectively in silos 20, 21 and 22 (Fig. 2).

This tobacco is supplied batch-wise to a contra-rotating double-screw mixer 23 wherein the tobacco is mixed with the relevant other ingredients, for example with the calcium alginate (see below), with an aqueous solution of the adhesive binder which solution is derived from a make-up tank 24 provided with a stirrer 25 and supplied with (a) process water via a control valve 26 and a flowmeter 27 and with (b) the adhesive binder(s) from a silo or silos 28, 29, and with any extra ingredients (humectant, flavour(s), colouring material, filler(s), etc.) from silos 30, 31. (The silos 20—22, 28, 29, 30 and 31 may supply appropriate weight-batcher devices 34, 32, 33, as indicated).

The calcium alginate, stored in a silo 50, is supplied batch-wise to the mixer 23 via an appropriate weight-batcher device 51. Again, the arrangement is such that the divided calcium alginate in the aqueous slurry (mix) formed by the mixer 23 comprises fibres or fibrous material or material derived by mechanical division of fibres or fibrous material.

The slurry (mix) thus formed within the mixer 23 is fed batch-wise, via an outlet valve 32, to the rolling-mill sequence indicated in Fig. 2. In the sequence shown there are five rolling-mill stands, 35—39 inclusive, arranged in sequence. Within the stand 35 the material is passed through the nip of a roll-pair and thereafter sequentially through the two nips of a trio of rolls. Within each of the stands 36—39 inclusive the material is passed sequentially through the three nips of a 4-high roll-arrangement.

From the stand 39 the rolled material passes, similarly to Fig. 1, to a similar support surface in the form of an endless moving belt 40 whereon the material is conveyed, as before, to and past suitable drying apparatus 41. As before, the material may then be reeled into a roll, or may be shredded (or otherwise mechanically divided) into small pieces (for example, flakes) by means of a suitable device 42.

This material may be used, in known general manner, to form binders or wrappers or filler material or the like for smoking articles such as pipes, cigarettes, cigars and the like.

In the cases where the said product material does not include tobacco and/or does not include an adhesive binder and/or where the alginate is not calcium alginate, the procedure is generally similar to that just described, with modifications as appropriate.

## EXAMPLE 2.

(a) 100% calcium-alginate paper sheet was first prepared by papermaking methods of the general kind described in our British patent specifications Nos. 1,372,510 and 1,370,888.

Thus, 35 kgm of moist calcium-alginate raw material (grade CA—33, ex Alginate Industries Ltd, see below) was charged to a pulp beater with sufficient water to produce a 6% consistency. The steam jacket was used to produce and maintain a pulp temperature of 35°C. The charge was beaten for 15 mins. to a freeness of 15° Schopper-Riegler, and then 360 gms. paper makers Alum (aluminium sulphate) was added as pH control agent to give a pH of 6.5. Beating was continued for a further 25 minutes to a freeness of 24° Schopper-Riegler, and the stock transferred to the machine chest where it was diluted to 2% consistency. This stock was run via the dilution box onto a pilot scale papermaking machine, bypassing the refiner, set to the conditions listed below. Processing was extremely easy, typical in-process readings

as given below being obtained. The product was a yellow-brown coherent sheet of excellent quality, at ca.100 gm/m² dry weight. There was a shrinkage of ca.18% through the machine.

The product was reeled from the machine at approximately 20% moisture content.

The paper-making machine was run under the following conditions:

*Machine settings*

1) Flow to wire: 22 litres per minute.
2) Machine speed: 20ft/minute linear wire speed.
3) Shake stroke amplitude: 3/16".
4) Felt tensions: all at 400 p.s.i.
5) Nip pressures: all at 600 p.s.i.
6) Drying cylinder steam pressures and recorded consequent temperatures during running were as follows:

| Drying Cylinder No: | | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
|---|---|---|---|---|---|---|---|---|---|---|
| Steam pressure (p.s.i.) | (vacuum) | | 3 | 2 | 2 | 8 | off | 0 | 0 | 0 |
| Approx. Cylinder Temperature (°C) | | 48 | 88 | 90 | 92 | 100 | off | 65 | 55 | 70 |

(No. 6 cylinder was not working during the run, but this did not affect the processing).

With the machine settings as above, the following were typical readings obtained at various points throughout the process during running:

1) White water: 40 litres per minute.
2) 1st Box vacuum: 4 inches mercury.
3) 2nd Box vacuum: 4 inches mercury.
4) 3rd Box vacuum: 3.5 inches mercury.
5) Kopp: 16.
6) Couch vacuum: 4 inches mercury.

(b) This paper sheet material, consisting of substantially 100% calcium alginate in fibrous form, was shredded to 52 cuts per inch, when it had a moisture-content of about 20%, and was utilised as described below.

According to the required composition of the finished sheet (see Table 1 below), the required quantities of ground tobacco offal, the calcium-alginate shredded sheet, an adhesive binder (the sodium salt of carboxymethyl cellulose in aqueous solution), and an humectant (diethyleneglycol), were well mixed in the contra-rotating double-screw mixer 23, together with further water (additional to that used to dissolve the binder) sufficient to plasticize the mixture suitably for the roll-processing. (The weight of the water added was generally less than 50% of the weight of the tobacco offal).

When sufficiently mixed, the material was conveyed (via an electro-magnet 52 to remove metallic particles) to the first of the rolling-mill stands at which the material was passed through the first roll-nip. The roughly-formed and self-supporting wet sheet thus obtained, did not adhere to the surface of the rolls and was passed to the second roll-nip. The roughly-formed sheet thus obtained was conveyed, still wet, to the subsequent 4-high rolling-mills at which the material was passed through the roll-nips in turn.

The sheet issuing from the last of the rolling-mills was still wet and was of low tensile strength, and it was dried by passage through an in-line infra-red oven 41, to yield a self-supporting, good-quality sheet having a basis-weight of about 80 gm/m². The added calcium-alginate shredded sheet was distributed evenly through the product sheet, producing a "speckled" colouration effect which was even.

Sheets of the following compositions were produced:—

Table 1.

(All percentages are based on the final weight of the product sheet.)

| % Calcium Alginate Sheet | % Tobacco Offal | % (Carboxymethyl Cellulose, Sodium Salt) Binder | % Humectant (Diethyleneglycol) |
|---|---|---|---|
| 6 | 87 | 5 | 2 |
| 12 | 81 | 5 | 2 |
| 18 | 75 | 5 | 2 |
| 30 | 63 | 5 | 2 |
| 50 | 43 | 5 | 2 |
| 75 | 18 | 5 | 2 |

*The calcium alginate (or other alginate) raw material.*

Where the product material is to be used in or as smokeable material, the produced mix is to include divided *calcium* alginate comprising fibres or fibrous material or material derived by mechanical division of fibres or fibrous material.

The expression "raw fibrous calcium alginate material" is conveniently used herein to denote calcium alginate raw material in the form of fibres, fibre-bundles and the like, as obtained by squirting an aqueous solution of water-soluble alginate into a solution of an inorganic salt whose cation will react with the water-soluble alginate to produce the "raw fibrous calcium alginate material". Customarily, the squirting is via a spinneret, the aqueous solution of water-soluble alginate is derived in known manner from seaweed, and the inorganic salt is calcium chloride; and such "raw fibrous calcium alginate material" is commercially available in the U.K. (see below) as grade CA—33, in the form of fibre-bundles, as supplied by Alginate Industries Ltd.

Such "raw fibrous calcium alginate material", having been water-washed if necessary to purify it, may be directly present in the mix of the *present* invention. The divided calcium alginate in the mix may thus comprise such fibres or fibrous material. Alternatively, the purified "raw fibrous calcium alginate material" may be mechanically divided to reduce the material to a suitable small or smaller size in which it then appears in the mix as the said material derived by mechanical division of fibres or fibrous material.

The procedure of two paragraphs above may be as follows. Harvested cut seaweed may be dried and milled (in any order), this step reducing the seaweed to an easily-handled form in which it may be stored before processing and in which it is less likely to suffer biological degradation. (The seaweed may also be washed, at this stage). The seaweed is then treated with alkali and water: for example, it may be treated with an aqueous solution of sodium carbonate (with or without caustic soda) whereby the alginate in the seaweed is converted into water-soluble sodium alginate in a crude alginate solution wherein the solid impurities may be allowed to settle as a sediment. The supernatant liquid may then be squirted through the spinneret into an aqueous calcium-chloride solution to thereby precipitate crude calcium alginate I in fibrous form.

Such crude calcium alginate I in fibrous form may be directly or otherwise incorporated into the slurry (mix) of the present invention: however, such crude calcium alginate tends to have a strong odour which may make it unacceptable in smoking material and, therefore, in such circumstances the calcium alginate may first be "repurified". Thus, the crude calcium alginate may be skimmed off, and squeezed to remove surplus water. It is then reacted with suitable aqueous acid to yield a precipitate of water-insoluble alginic acid which is skimmed off, and pressed to remove surplus water. The resulting material is then dissolved in an aqueous solution of sodium carbonate to form a sodium-alginate solution which, as before, is squirted through a spinneret into an aqueous calcium-chloride solution to thereby precipitate calcium alginate II in the fibrous form (referred to herein as type CA—33).

Our U.K. patent specification No. 1,370,888 provides and claims an alginate (e.g. calcium alginate) paper consisting essentially of raw water-insoluble alginate (e.g. calcium alginate) fibres which are held together to form the (paper) sheet material without the use or formation of an additional adhesive binder or swelling agent. The specification also provides and claims a method of manufacturing such sheet material, by specified steps including the use of the web-forming unit of a papermaking machine, from raw fibrous water-

insoluble alginate (e.g. calcium alginate) material as obtained by squirting an aqueous solution of water-soluble alginate into a solution of an inorganic salt whose cation will react with that (water-soluble) alginate to produce (the) water-insoluble alginate (e.g. calcium alginate).

Such *calcium* alginate (paper) sheet material may be mechanically divided (conveniently while dry or substantially dry) to reduce the material to a suitable small or smaller size in which it then appears in the mix (of the *present* invention) as the said material derived by mechanical division of fibres or fibrous material.

Our U.K. patent specification No. 1,370,888 further indicates and claims that a filler or solid diluent (e.g. wood pulp) may be incorporated into the (paper) sheet material. Such *calcium* alginate (paper) sheet material, loaded in this way with (see below) a suitable filler or solid diluent, may be mechanically divided (conveniently while dry or substantially dry) to reduce the material to a suitable small or smaller size in which it then appears in the mix (of the *present* invention) as the said material derived by mechanical division of fibres or fibrous material.

Such suitable filler materials include kaolin, or calcium carbonate, or, more generally, materials defined as follows:—

*Materials useful as Fillers.*

There are many materials which are well-known and used as fillers. However, in the case of smokeable materials, constraints are imposed by the need not to use poisonous materials or materials with undesirable combustion products. Some suitable fillers are, subject to the limitations above,

(i) Rock, clays, minerals, or earths, either naturally occurring or in any processed or manufactured form.

(ii) Insoluble industrial process wastes (e.g. Pulverised Fuel Ash).

(iii) Various inorganic compounds well-known in the paper, smoking material, or tobacco Art, e.g. Calcium Carbonate, Titanium Dioxide, Calcium Hydroxide, Aluminium Hydroxide, and Aluminium Carbonate.

Where the divided alginate in the mix is not calcium alginate, similar considerations apply.

## ADHESIVE BINDER

As the adhesive binder, at least in the case where the said product material is used in or as smokeable material, we prefer a water-soluble derivative (for example the sodium or another alkali metal salt or the ammonium salt) of carboxymethyl cellulose and/or another water-soluble adhesive binder (for example, methyl ether of cellulose, ethyl ether of cellulose, gelatin, or polyvinyl alcohol). We contemplate that the adhesive binder shall not be an alginate material. The process according to the invention may be so carried out that the pH of the slurry (mix) and/or of the thin layer (mass) is maintained at or below pH 7.0.

On the other hand, in certain cases we contemplate that the adhesive binder may be or include a water-soluble alginate material, for example sodium and/or potassium alginate.

In modifications, the adhesive binder may be other than a water-soluble adhesive binder (for example, carboxymethyl cellulose).

## GENERAL

The process for the manufacture of the sheet according to the invention may be arranged, for example by suitable mechanical modifications to the process equipment and/or by varying or modifying the processing conditions, to impart desirable physical characteristics to the sheet. Thus, for example, the sheet may be arranged to be creped, crimped, or embossed, or it may be "cockled" (the expression used in the textile industry) for instance by differential drying effects acting throughout the sheet thickness.

The process for the manufacture of sheet according to the invention is distinguished from a paper-making process in that much less water is used than in paper-making, and no screen (wire) is provided whereat water is removed to permit wet-felting of the fibres being made into sheet.

## CALCIUM ALGINATE

The incorporation of calcium alginate into product sheet of the invention and intended as a smokeable material, gives desirable improvements to the final product, as follows:—

(i) The product sheet has a lower basis-weight and increased tensile strength, as compared with reconstituted tobacco sheet from which the calcium alginate is absent. (Both of these properties are important, from the points of view of further processing and of filling-power).

(ii) The product sheet has improved porosity, and improved free-burning characteristics.

(iii) The product sheet has a desirable "speckled" surface-finish, and a lighter colour than otherwise.

(iv) We believe that the tobacco in the product sheet will have been diluted by a material which has improved combustion properties, i.e. we believe that the product sheet will have an improved smoke chemistry.

## WHAT WE CLAIM IS:—

1. A method of manufacturing product material including the steps of producing a mix including a water-soluble alginate in a divided state and liquid medium, forming a thin (as hereinbefore defined) elongate mass from the mix by means not including the use

of a web-forming unit of a paper-making machine and removing any surplus of the liquid medium from the thin mass, whereby to form with a required moisture-content the product material, in which the divided alginate comprises fibres or fibrous material or material derived by mechanical division of fibres or fibrous material.

2. A method according to Claim 1, wherein the liquid medium is water.

3. A method according to Claim 1 or Claim 2, wherein the mix contains also an adhesive binder.

4. A method according to any preceding claim, wherein the product material comprises sheet material.

5. A method according to any one of Claims 1—3, wherein the product material comprises filament material.

6. A method according to any preceding Claim, wherein the water-insoluble alginate is calcium alginate.

7. A method according to Claim 6 which includes the step of incorporating into the product material at any stage of the manufacture or subsequently, additional material so as at least to flavour the product material and to improve its burning characteristics.

8. A method according to Claim 7, wherein at least some of the additional material is incorporated into the mix.

9. A method according to Claim 7 or Claim 8, wherein the additional material consists of or includes tobacco in a divided state.

10. A method according to Claim 9, wherein the tobacco is present in the mix with a particle-size of the order of magnitude of 50 microns.

11. A method according to any one of Claims 7—10, wherein the additional material comprises at least one of a filler, an humectant, a colouring agent, an agent for supplying nicotine, an agent for modifying the action of nicotine, an agent for flavouring, an agent for sustaining burning, a combustion catalyst, a plasticizer, a wetting agent, a hardener.

12. A method according to any preceding Claim, wherein at least a part of the any surplus liquid medium is removed with the aid of heat.

13. A method according to any preceding Claim, wherein at least a part of the any surplus liquid medium is removed without the aid of heat.

14. A method according to any preceding Claim, wherein the mix is poured, as a step of forming the product material.

15. A method according to any one of Claims 1—13, wherein the mix is extruded, as a step of forming the product material.

16. A method according to any preceding Claim, wherein the mix is metered on to a support surface to form the thin mass, and the any surplus liquid medium is then removed so as to convert the thin mass into a self-supporting form.

17. A method according to any one of the Claims 1—13, wherein the material of the mix is converted by passage between rolls into a self-supporting form, the liquid medium incorporated into the mix being sufficient to permit such conversion.

18. A method according to any preceding Claim, wherein the mechanical division of fibres or fibrous material is by pulverization.

19. A method according to Claim 18, wherein the pulverized material has a particle-size of the order of magnitude of 50 microns.

20. A method according to any preceding Claim, wherein the divided alginate comprises fibres or fibrous material, as obtained by squirting an aqueous solution of water-soluble alginate into a solution of an inorganic salt whose cation will react with the water-soluble alginate to produce such fibres or fibrous material.

21. A method according to any preceding Claim, wherein at least some of the material derived by mechanical division is so derived from fibres or fibrous material, as obtained by squirting an aqueous solution of water-soluble alginate into a solution of an inorganic salt whose cation will react with the water-soluble alginate to produce such fibres or fibrous material.

22. A method according to any preceding Claim, wherein at least some of the material derived by mechanical division is so derived from fibrous sheet material.

23. A method according to Claim 22, wherein the fibrous sheet material is made from fibres or fibrous material, as obtained by squirting an aqueous solution of water-soluble alginate into a solution of an inorganic salt whose cation will react with the water-soluble alginate to produce such fibres or fibrous material.

24. A method according to any one of Claims 20, 21 and 23, in each case as directly or indirectly dependent upon Claim 6, wherein the solution of an inorganic salt comprises an aqueous solution of calcium chloride.

25. A method according to any one of Claims 20, 21, 23 and 25, wherein the aqueous solution of water-soluble alginate is as obtained in generally known manner from seaweed.

26. A method according to any preceding Claim, wherein at least some of the mechanical division is performed upon the fibres or fibrous material while substantially dry and prior to introduction to the mix.

27. A method according to Claim 3 or any Claim dependent upon Claim 3, wherein the adhesive binder is not an alginate material.

28. A method according to any preceding Claim, which is so carried out that the pH of the mix and/or of the thin mass is main-

tained at or below pH 7.0.

29. A method according to Claim 3 or any Claim dependent upon Claim 3, wherein the adhesive binder is water-soluble.

30. A method according to Claim 29, wherein the adhesive binder is or includes a water-soluble derivative of carboxymethyl cellulose.

31. A method according to Claim 3 or any one of Claims 4—26 when dependent upon Claim 3, wherein the adhesive binder is or includes a water-soluble alginate material.

32. A method according to Claim 31, wherein the adhesive binder is or includes sodium alginate and/or potassium alginate.

33. A method according to Claim 3 or any one of Claims 4—28 when dependent upon Claim 3, wherein the adhesive binder is other than a water-soluble adhesive binder.

34. A method according to Claim 3 or any Claim dependent upon Claim 3, wherein the adhesive binder is at least in part water-soluble to form aqueous material having at its introduction to the mix a relatively low viscosity of the order of magnitude of 50 centipoises.

35. A method according to Claim 4 or any claim dependent upon Claim 4, wherein the product material is creped, crimped, embossed or cockled.

36. A method according to any preceding Claim, wherein the product material is shredded or otherwise mechanically divided.

37. A method of manufacturing product material, substantially as specifically described herein in Example 1(A), or Example 1(B), or Example 2(b) with or without Example 2(a).

38. The product material manufactured according to the method as claimed in any one of Claims 1—37.

39. Smokeable material which comprises product material manufactured according to the method as claimed in Claim 6, or as claimed in any one of Claims 7—36 when dependent upon Claim 6.

40. Smokeable material which comprises product material manufactured according to the method as claimed in Claim 37.

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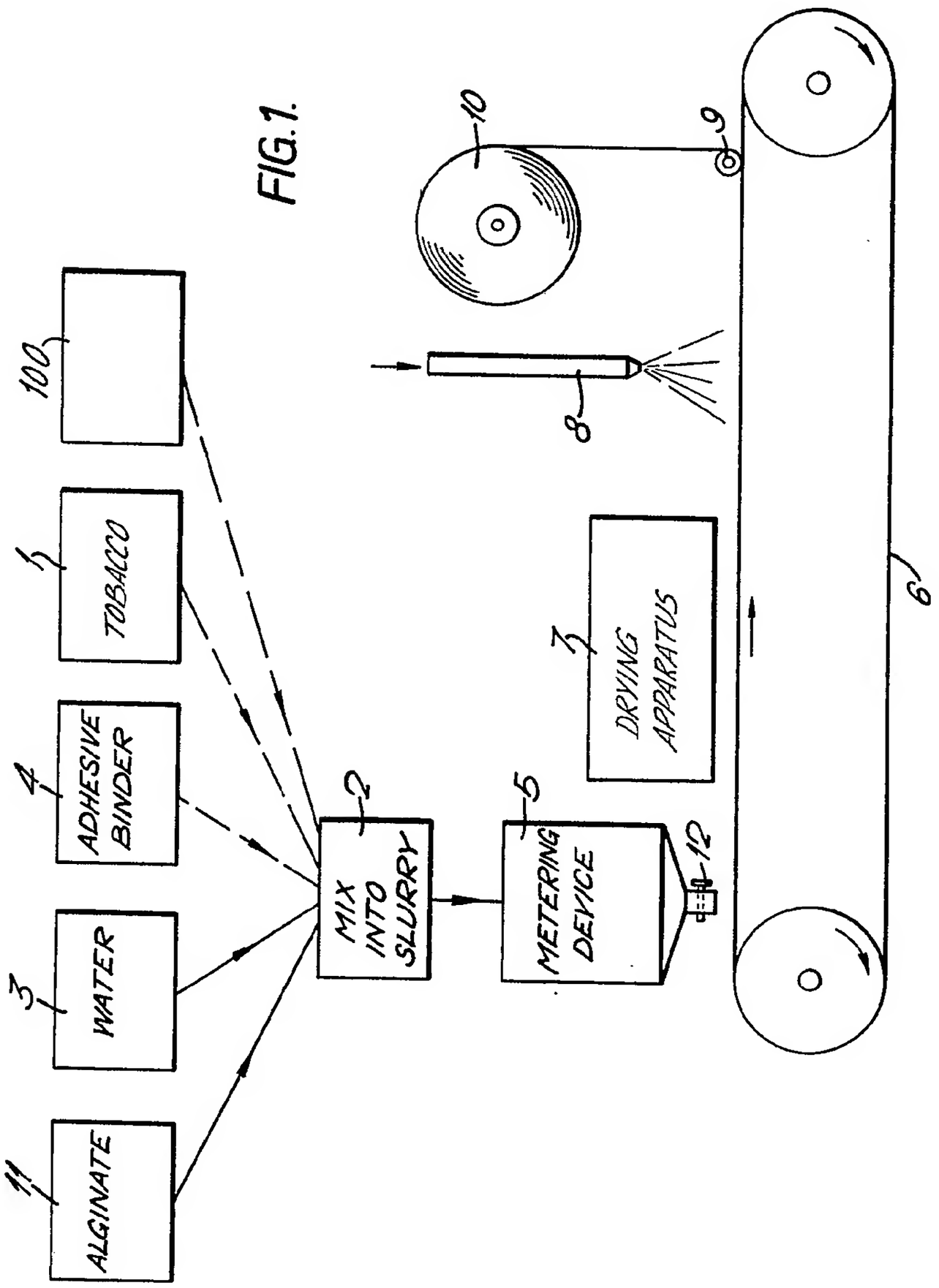
FIG.1.



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**Sheet 2**

FIG. 2.